

## Electronic and structural properties of NaZnX (X = P, As, Sb): an *ab initio* study

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2008 J. Phys.: Condens. Matter 20 085220

(<http://iopscience.iop.org/0953-8984/20/8/085220>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 29/05/2010 at 10:36

Please note that [terms and conditions apply](#).

# Electronic and structural properties of NaZnX (X = P, As, Sb): an *ab initio* study

G Jaiganesh<sup>1</sup>, T Merita Anto Britto, R D Eithiraj and G Kalpana

Department of Physics, Anna University-Chennai, Chennai-600 025, India

E-mail: [jai\\_spectrum@yahoo.com](mailto:jai_spectrum@yahoo.com)

Received 21 November 2007, in final form 14 January 2008

Published 7 February 2008

Online at [stacks.iop.org/JPhysCM/20/085220](http://stacks.iop.org/JPhysCM/20/085220)

## Abstract

The first-principles tight-binding linear muffin-tin orbital method within the local density approximation (LDA) has been used to calculate the ground-state properties, structural phase stability and pressure dependence of the band gap of NaZnX (X = P, As, Sb). All three compounds are found to crystallize in the tetragonal Cu<sub>2</sub>Sb-type (C38) structure. NaZnAs is also found to crystallize in the zinc-blende-type related structure, i.e. the MgAgAs (order CaF<sub>2</sub>)-type structure. By interchanging the position of the atoms in the zinc-blende structure, three phases ( $\alpha$ ,  $\beta$  and  $\gamma$ ) are formed. The energy–volume relations for these compounds have been obtained in the Cu<sub>2</sub>Sb-type and cubic  $\alpha$ ,  $\beta$  and  $\gamma$  phases of the zinc-blende-type related structure. Under ambient conditions these compounds are more stable in the Cu<sub>2</sub>Sb-type structure and are in agreement with experimental observations. At high pressure, these compounds undergo a structural phase transition from the tetragonal Cu<sub>2</sub>Sb-type to cubic  $\alpha$  (or  $\beta$ ) phase, and the transition pressures were calculated. The equilibrium lattice parameter, bulk modulus and the cohesive energy for these compounds have also been calculated and are compared with the available results. In the Cu<sub>2</sub>Sb-type structure, NaZnP is found to be a direct-band-gap semiconductor, NaZnAs shows a very small direct band gap and NaZnSb is found to be a metal. In the  $\alpha$  and  $\beta$  phases, NaZnP is found to be a direct-band-gap semiconductor, whereas NaZnAs and NaZnSb are found to be semi-metallic. In the  $\gamma$ -phase, all three compounds are found to exhibit metallic behaviour. However, this phase is energetically unfavourable.

## 1. Introduction

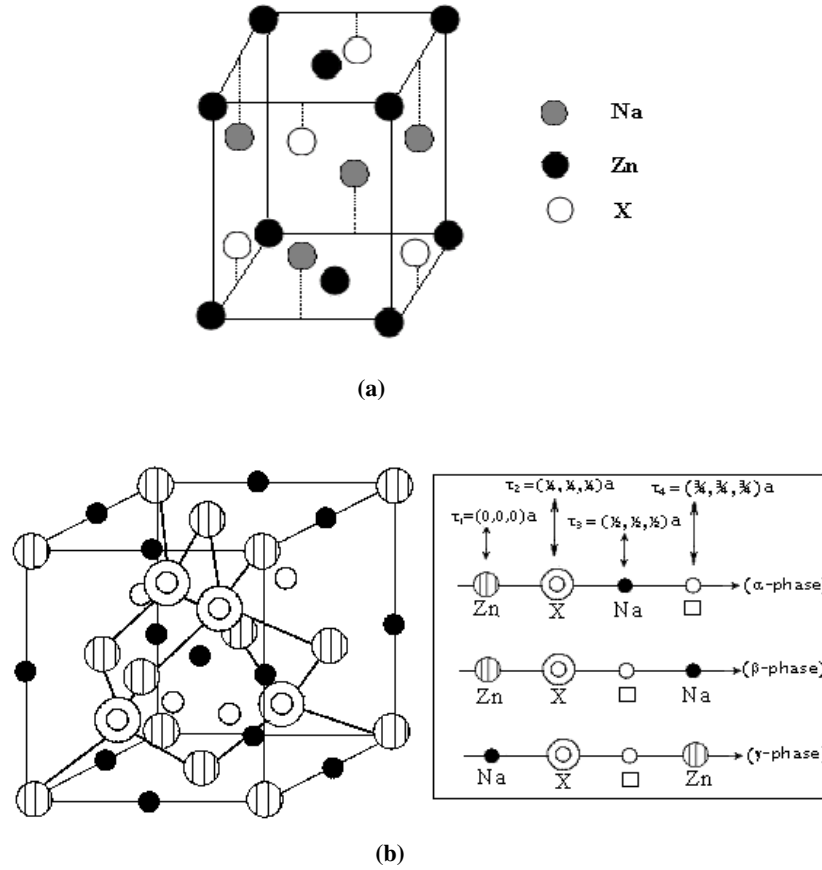
The Nowotny–Juzza compounds A<sup>I</sup>B<sup>II</sup>C<sup>V</sup> (A<sup>I</sup> = Li, Na, Cu, Ag; B<sup>II</sup> = Mg, Zn and C<sup>V</sup> = N, P, As, Sb and Bi) have been synthesized, mostly in the 1940s, but have been characterized only in terms of their crystal structure and colours. They are semiconductors which belong to the class of filled tetrahedral compounds (FTC), recognized as promising materials for technological applications [1–5].

Generally, the crystal structure of Nowotny–Juzza compounds can be derived from the zinc-blende III–V compounds by transmuting the group III atom into an isovalent pair I + II, and are found to crystallize mostly in cubic zinc-blende-type related structures [6, 7]. NaZnX (X = P, As, Sb) forms a special case, which is found to crystallize in tetragonal Cu<sub>2</sub>Sb-type structure [8]. NaZnAs is also found to crystallize in the MgAgAs (order CaF<sub>2</sub>)-type structure [9]. NaZnP as a catalyst

has been proved to be extremely selective [10, 11]. NaZnP and NaZnSb present antifluorite two-dimensional (2D) building blocks that have similar in-plane parameters and complementary electron acceptor characteristics [12–14]. Unfortunately, there is little data concerning the lattice parameters and cohesive energies of these compounds [8, 13]. Yet, up to now, there has been no theoretical work concerning the electronic, structural and physical properties of NaZnX, although their potential technological applications have been emphasized.

In this paper, we describe the results of the first-principles electronic structure calculations of NaZnX (X = P, As, Sb) compounds in the tetragonal Cu<sub>2</sub>Sb-type and cubic  $\alpha$  (MgAgAs-type),  $\beta$  and  $\gamma$  phases of zinc-blende-type related structures. The calculations are performed using the tight-binding linear muffin-tin orbital (TB-LMTO) method, within the atomic sphere approximation (ASA) [15, 16]. Due to the absence of experimental measurements on the properties of NaZnP, NaZnAs and NaZnSb compounds, the results were compared with LiZnX (X = P, As, Sb) and also the reliability

<sup>1</sup> Author to whom any correspondence should be addressed.



**Figure 1.** (a) Schematic diagram of the unit cell of NaZnX in primitive tetragonal Cu<sub>2</sub>Sb-type structure and (b) crystal structure (left panel) and atomic positions along the  $\langle 111 \rangle$  crystal direction (right panel) of the  $\alpha$ ,  $\beta$  and  $\gamma$  phases of cubic NaZnX compounds. Here,  $\square$  represents the empty site.

of our predicted results was checked. The rest of this paper is organized as follows: in section 2 we briefly discuss the crystal structure of NaZnX (X = P, As, Sb); in section 3 we describe the computational details of the calculations; in section 4 the obtained results are discussed. Finally, a conclusion is given in section 5.

## 2. Crystal structure

NaZnX (X = P, As, Sb) is found to crystallize in tetragonal Cu<sub>2</sub>Sb-type structure, with the space group (129)  $P4/nmm$  [8]. The Cu<sub>2</sub>Sb-type structure is illustrated in figure 1(a). In the Cu<sub>2</sub>Sb-type crystal lattice of NaZnX, there are two kinds of cation sites, namely the Zn and Na sites, which are surrounded tetrahedrally and octahedrally by X (X = P, As, Sb) atoms, respectively. The unit cell contains two molecules per formula unit. The Zn atoms are at positions (0, 0, 0) and (1/2, 1/2, 0). The Na and X (X = P, As, Sb) atoms are at the positions (0, 1/2, z) and (1/2, 0, -z) and the values of the z-parameters for Na and X are given in table 1. For NaZnAs, the z-parameters are not available. We have optimized the z-parameter for NaZnAs. For NaZnP and NaZnSb, experimental z-parameter values are used in calculations [8].

Generally, in the Cu<sub>2</sub>Sb-type structure only one empty sphere is used; in our calculations for NaZnX (X = P, As, Sb)

**Table 1.** z-parameter for NaZnX compounds.

Na:	0.3590	Na:	0.3592	Na:	0.653
P:	0.7873	As:	0.7885	Sb:	0.221

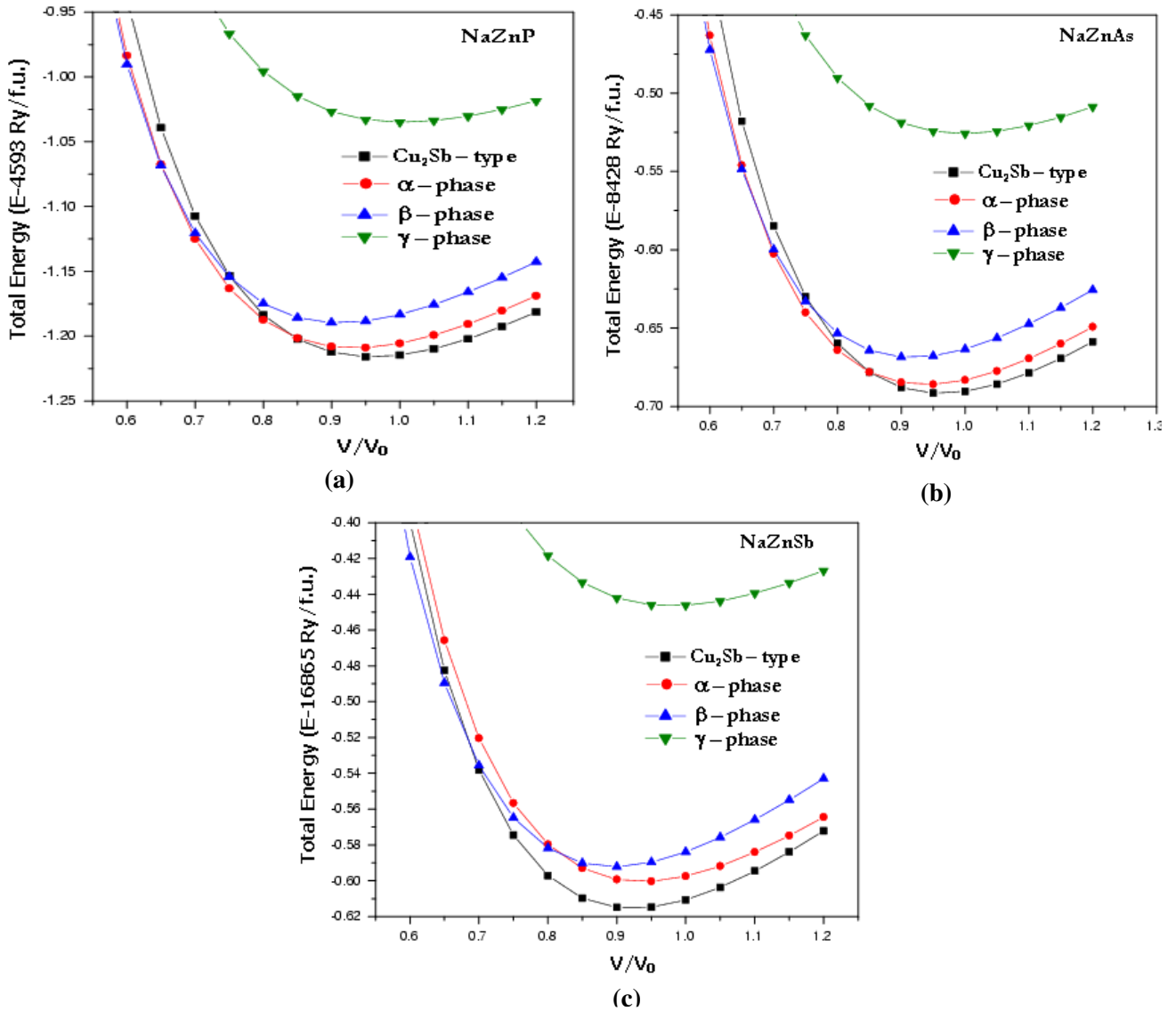
compounds, six empty spheres are introduced into the unit cell since there are two kinds of cations with different atomic sizes. The empty spheres are placed at the positions

$$E_1: (0, 0, 0.84); \quad (1/2, 1/2, 0.84)$$

$$E_2: (0, 0, +0.42); \quad (0, 0, -0.42)$$

$$E_3: (1/2, 1/2, +0.42); \quad (1/2, 1/2, -0.42).$$

In the zinc-blende-type related structure, A<sup>I</sup>B<sup>II</sup>C<sup>V</sup> compounds may be viewed as follows: D<sup>III</sup>-C<sup>V</sup> compounds (e.g. GaAs) in the zinc-blende structure have the D<sup>III</sup> atom at the sublattices  $\tau_1 = (0, 0, 0) a$  (where  $a$  is the lattice parameter), the C<sup>V</sup> atom at  $\tau_2 = (1/4, 1/4, 1/4) a$  and two empty interstitial sites at  $\tau_3 = (1/2, 1/2, 1/2) a$  next to the anion and  $\tau_4 = (3/4, 3/4, 3/4) a$  next to the cation. One could transmute the D<sup>III</sup> atom into its isovalent pair B<sup>II</sup> + A<sup>I</sup> by inserting a closed-shell atom like He, Li, Na... in one of the empty sites (e.g. Ga into Zn + Na) and distributing these among the  $\tau_1$ ,  $\tau_3$  and  $\tau_4$  sites. This is shown in figure 1(b). There are three distinct



**Figure 2.** Total energy per molecule as a function of relative volume for the tetragonal  $\text{Cu}_2\text{Sb}$ -type and  $\alpha$ -,  $\beta$ - and  $\gamma$ -phases of  $\text{NaZnX}$  ( $X = \text{P}, \text{As}, \text{Sb}$ ).

(This figure is in colour only in the electronic version)

ways of periodically distributing three atoms A, B and C on the four sublattices  $\tau_1, \tau_2, \tau_3$  and  $\tau_4$ , and the resultant structures are denoted as  $\alpha$  ( $\text{ZnXNa}\square$ ),  $\beta$  ( $\text{ZnX}\square\text{Na}$ ) and  $\gamma$  ( $\text{NaX}\square\text{Zn}$ ) phases of the cubic  $\text{A}^{\text{I}}\text{B}^{\text{II}}\text{C}^{\text{V}}$  compounds. The symbol  $\square$  means a vacant site and technically, in connection with the LMTO method, an ‘empty sphere’. The cubic  $\alpha$ -phase is also denoted as the  $\text{MgAgAs}$  (ordered  $\text{CaF}_2$ )-type structure [9].

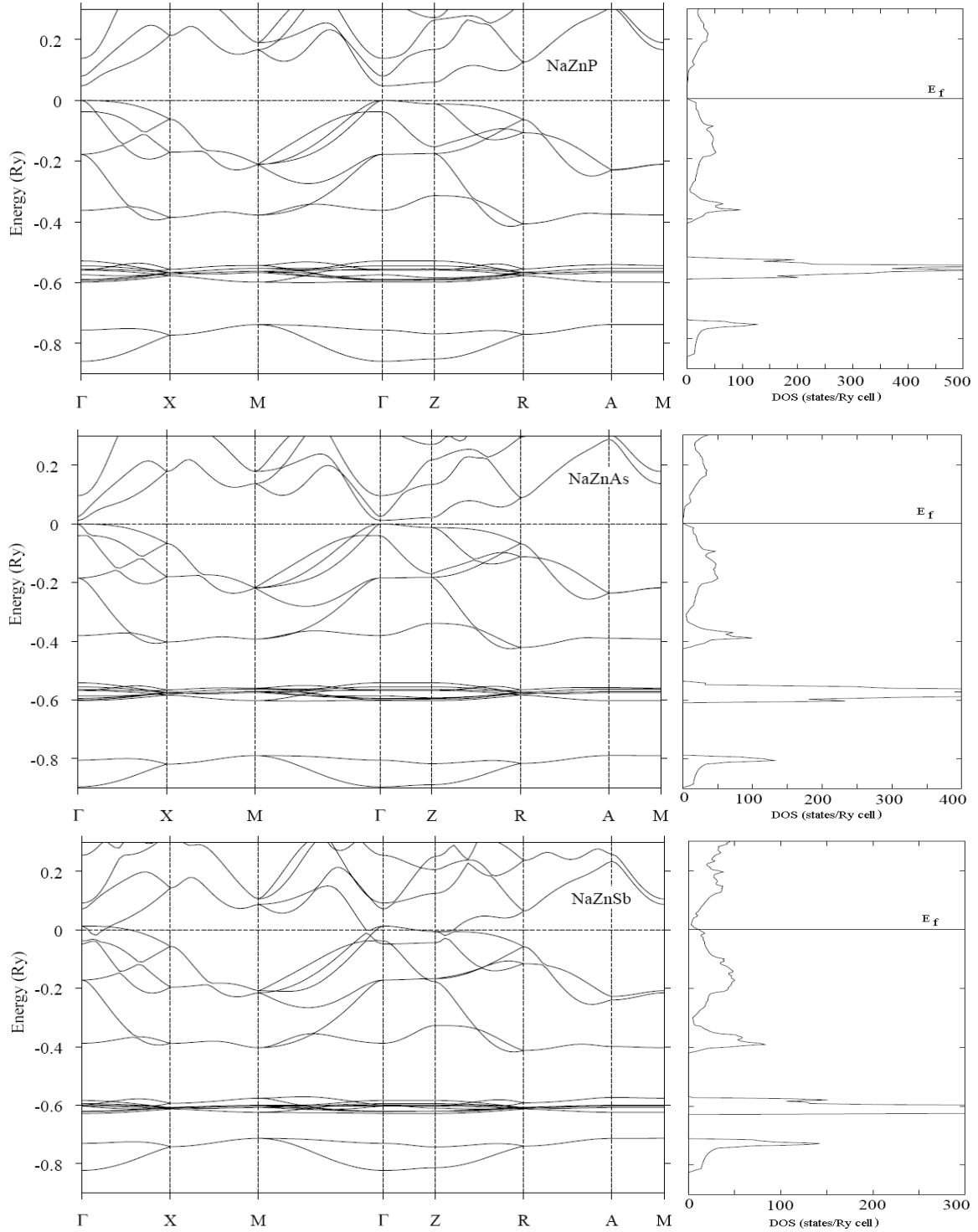
### 3. Theoretical frame work

The electronic structure of  $\text{NaZnX}$  ( $X = \text{P}, \text{As}, \text{Sb}$ ) has been investigated through first-principles calculations by using the efficient computational scheme offered by Andersen’s tight-binding linear muffin-tin orbital (TB-LMTO) method. This method has been described well in the literature [15, 16].

In the atomic sphere approximation (ASA), the interstitial region of the muffin-tin starting potential is annihilated through

the expansion of the muffin-tin spheres and the neglect of the slight overlap. The muffin-tin spheres in this approximation thus become the Wigner–Seitz spheres, which fill all the space. The potential is taken to be spherically symmetric within the spheres. In this work, the Wigner–Seitz sphere radii are chosen in such a way that the potential discontinuity at the sphere boundary is a minimum and the charge flow between the atoms is in accordance with the electro-negativity criteria. We have kept the maximum overlap between the spheres as approximately 16%.

In this method, the total energy and electronic structure calculations were performed on the basis of the density functional theory (DFT) within the local density approximation (LDA) [17, 18]. Exchange and correlation contributions to both the atomic and crystalline potentials have been included through the von Barth–Hedin scheme [19]. The density of



**Figure 3.** Electronic band structure (left panel) and total density of states (right panel) of NaZnX in the tetragonal  $\text{Cu}_2\text{Sb}$ -type structure at their equilibrium volume. The energy zero is chosen to be at the Fermi energy  $E_F$ .

states (DOS) was calculated by the tetrahedron method [20]. In this method the  $\mathbf{k}$ -point grid, where eigenvalues are computed, defines a set of tetrahedral micro-zones. The contribution of each micro-cell to the density of states is computed from a linear interpolation based on the energies at the corners of the micro-zone, for each band. The Brillouin zone (BZ) integration is performed by the usual tetrahedron technique.

We use 1496  $\mathbf{k}$ -points and 1368  $\mathbf{k}$ -points in the irreducible part of the Brillouin zone to construct the tetrahedrons in the tetragonal  $\text{Cu}_2\text{Sb}$ -type and cubic ( $\alpha$ ,  $\beta$ ,  $\gamma$ ) structures, respectively.

In this work, we treat the core electrons fully relativistically and the valence electrons semi-relativistically (all the relativistic effects are taken in account except for the

**Table 2.** Lattice parameter ( $a$ ,  $c$ ) in Å, cohesive energy ( $E_{\text{coh}}$ ) in eV per formula unit, and bulk modulus ( $B_0$ ) in GPa for NaZnX ( $X = \text{P, As, Sb}$ ).

Structure	NaZnP			NaZnAs		NaZnSb	
	Expt. <sup>a</sup>	Present	VASP <sup>b</sup>	Expt. <sup>a</sup>	Present	Expt. <sup>a</sup>	Present
$a$	4.066	4.012	4.0673	4.176	4.1217	4.442	4.365
$c/a$	1.6953	1.6952	—	1.6973	1.6972	1.6866	1.6868
$\text{Cu}_2\text{Sb}$	$E_{\text{coh}}$	—	-10.3379	-9.098	—	-9.7057	—
	$B_0$	—	124.85	—	—	111.95	—
	$a$	—	5.7501	—	5.912	5.9167	—
$\alpha$ -phase	$B_0$	—	122.62	—	—	107.11	—
							86.91

<sup>a</sup> References [8, 9].<sup>b</sup> Reference [13].**Table 3.** Total energy differences between the tetragonal  $\text{Cu}_2\text{Sb}$  and cubic  $\alpha$ -,  $\beta$ - and  $\gamma$ -phases.

Compounds	Total energy difference (Ryd/f.u.)		
	$E_t - E_\alpha$	$E_t - E_\beta$	$E_t - E_\gamma$
NaZnP	-0.0068	-0.0270	-0.1120
NaZnAs	-0.0056	-0.0229	-0.1658
NaZnSb	-0.0149	-0.0232	-0.1690

spin-orbit coupling). In the calculations, the following basis orbitals were used:

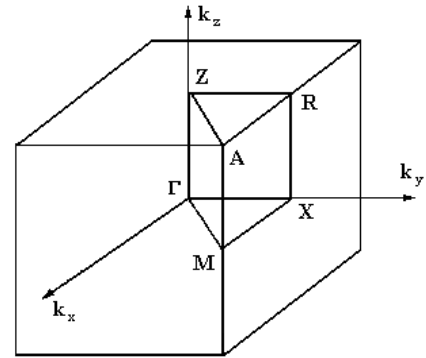
Elements	Orbitals		
Na	$3s^1$	$3p^0$	$3d^0$
P	$3s^2$	$3p^3$	$3d^0$
As	$4s^2$	$4p^3$	$4d^0$
Sb	$5s^2$	$5p^3$	$5d^0$
Zn	$4s^2$	$4p^0$	$3d^{10}$

## 4. Results and discussions

### 4.1. Total energy and related properties

In the TB-LMTO calculation, the total energy is a direct output. The total energy as a function of the relative volume was calculated in the tetragonal  $\text{Cu}_2\text{Sb}$ -type and cubic ( $\alpha$ -,  $\beta$ - and  $\gamma$ -phase) structures and is shown in figures 2(a)–(c). Also, the variation in the  $c/a$  ratio with total energy for all three compounds is studied. The value of the equilibrium  $c/a$  ratio is given in table 2. Also, the calculated equilibrium lattice parameters, bulk modulus and the cohesive energy of NaZnX compounds are summarized in table 2 together with the available data [8, 9] and [13]. The calculated bulk modulus decreases from NaZnP to NaZnSb, suggesting that the compressibility increases from NaZnP to NaZnSb.

The obtained total energy difference between the tetragonal  $\text{Cu}_2\text{Sb}$ -type ( $E_t$ ) and cubic  $\alpha$  ( $E_\alpha$ )-,  $\beta$  ( $E_\beta$ )- and  $\gamma$  ( $E_\gamma$ )-phases is given in table 3. From this data, this indicates that the tetragonal  $\text{Cu}_2\text{Sb}$ -type structure is the energetically favourable structure. Also, it is in good agreement with experimental observations. The energy difference between the two structures ( $\text{Cu}_2\text{Sb}$ -type and  $\alpha$ ) is small. This may be the reason why NaZnAs crystallizes in both structures. Compared

**Figure 4.** The first Brillouin zone (with symmetry lines and some symmetry points) of the primitive tetragonal lattice.

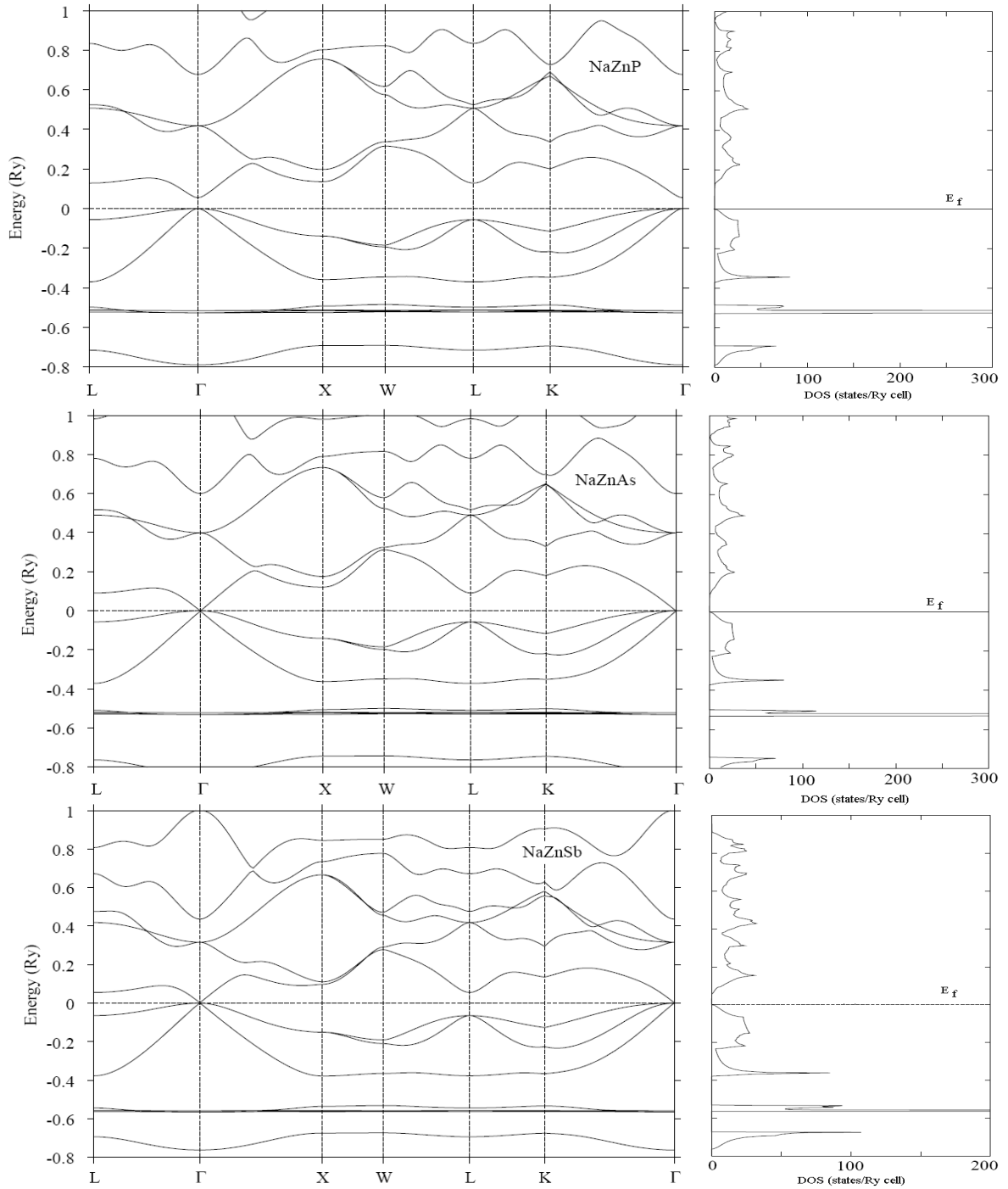
to other structures, the  $\gamma$ -phase has relatively high energy and is unstable.

The calculated total energies as a function of volume were fitted to the Birch equation of state [21]. There occurs a structural phase transition from  $\text{Cu}_2\text{Sb}$ -type to cubic  $\alpha$ -phase (or  $\beta$ -phase) at high pressure. The transition pressures are calculated at which the enthalpy of tetragonal  $\text{Cu}_2\text{Sb}$  phase equals that of the cubic  $\alpha$ -phase (or  $\beta$ -phase). The calculated phase transition parameters are listed in table 4.

### 4.2. Band structure and density of states

The electronic band structures and the densities of states of NaZnX ( $X = \text{P, As, Sb}$ ) were calculated in  $\text{Cu}_2\text{Sb}$ -type and cubic  $\alpha$ -,  $\beta$ - and  $\gamma$ -phases. Figures 3 and 5 illustrate the calculated band structures (left panel) and the corresponding total DOSs (right panel) for the three compounds studied in  $\text{Cu}_2\text{Sb}$ -type and cubic  $\alpha$ -phase. The band gap of these compounds in both structures is given in table 5.

The band structure profile in the tetragonal structure is described as follows. The calculated band structure for the ground state is shown in figure 3, which is drawn along the symmetry directions in the first Brillouin zone given in figure 4. The appearance of bands in this structure is due to the presence of two molecules per formula unit. The first peak reflects the group V atom 's'-like states, which correspond to the low-lying band in figure 3, and its width originates mainly from the region around the  $\Gamma$ -point in the Brillouin zone, since only



**Figure 5.** Electronic band structure (left panel) and total density of states (right panel) of NaZnX in the cubic  $\alpha$ -phase at their equilibrium volume. The energy zero is chosen to be at the Fermi energy  $E_F$ .

there is the dispersion of the band appreciable. The peak is centred around  $-0.75$ ,  $-0.8$  and  $-0.75$  Ryd for NaZnP, NaZnAs and NaZnSb, respectively. The next one shows a narrow Zn ‘d’-like state. From the partial density of states (not shown in the figure), we observe that this also contains a small contribution from the group V atoms’ ‘p’-like states, which decreases in the sequence NaZnP–NaZnAs–NaZnSb. The top-most valence band arises mainly from the group V atoms’ ‘p’-like states, which also contain a small amount of

‘s’- and ‘d’-like states of Na and Zn atoms. The contribution of ‘d’-like states to the valence band maximum (VBM) is larger in NaZnP than in the others. The low-lying conduction band arises predominantly from the ‘s’-like states of the Zn atom rather than the Na atom’s ‘s’-like states. Our calculation indicates that the VBM is at the  $\Gamma$ -point and that the minimum of the conduction band is also at the  $\Gamma$ -point for NaZnP and NaZnAs. The band structure profile of NaZnSb shows that this compound is metallic due to the overlapping of the Sb



**Table 4.** Calculated transition pressure values in GPa.

Compounds	Transition pressure ( $P_t$ ) GPa		
	Cu <sub>2</sub> Sb → $\alpha$ -phase	$\alpha$ → $\beta$ -phase	Cu <sub>2</sub> Sb → $\beta$ -phase
NaZnP	19.60	90.50	—
NaZnAs	15.75	72.40	—
NaZnSb	—	—	51.6

**Table 5.** Band gap  $E_g$  (eV) of NaZnX at equilibrium lattice parameter.

Compounds	Cu <sub>2</sub> Sb-type			
	Present	LAPW + lo method <sup>a</sup>	$\alpha$ -phase	$\beta$ -phase
NaZnP	0.64	—	0.75	0.66
NaZnAs	0.163	—	0.00	0.00
NaZnSb	0.00	0.00	0.00	0.00

<sup>a</sup> Reference [5].

'p'-like states and the Na and Zn '3s'-like states. The trend in the decrease of the band gap from NaZnP to NaZnSb is as follows: NaZnP is a direct-band-gap semiconductor with a band gap equal to 0.64 eV, whereas NaZnAs shows a direct band gap of 0.16 eV, which is less than the semiconductor range. NaZnSb is found to be a metal, and this is in agreement with available data [5]. NaZnP and NaZnAs exhibit band overlap metallization at compressions of 50% and 45% of the unit cell volume, respectively.

Figure 5 illustrates the band structure profile of NaZnX in the cubic  $\alpha$ -phase at their equilibrium volume, which shows a great resemblance to tetragonal Cu<sub>2</sub>Sb-type structure and which is in agreement with the overall band structure profile of LiZnX [22–24]. From the band-gap values listed in table 5 it can be seen that NaZnP is semiconducting in the cubic  $\alpha$ - and  $\beta$ -phases with direct band gaps of 0.75 eV and 0.66 eV respectively, whereas NaZnAs and NaZnSb show a semi-metallic nature with zero band gap. However, LDA is known to underestimate the band gap, and this underestimation is particularly large in the case of covalent crystals and may turn a small-band-gap semiconductor into a semi-metal. NaZnX in its  $\alpha$ - and  $\beta$ -phases are found to exhibit band overlap metallization upon compression. In the  $\gamma$ -phase, all three compounds were found to be metallic. The  $\alpha$ - and  $\beta$ -phases have identical relative arrangements of Zn and X atoms, which favours the formation of covalent Zn–X sp<sup>3</sup> bonds. This condition is the main factor in the formation of the semiconducting electronic structure. The actual position of Na atom is less important in that respect, whether it sits on sites  $\tau_3$  or  $\tau_4$  sites can hardly affect the band structure.

The third  $\gamma$ -phase is the one which mostly resembles that of CaF<sub>2</sub>, from which it may be derived by placing Na on the Ca positions. The arrangement of the Zn and X atoms in this case does not allow the formation of Zn–X sp<sup>3</sup> bonds. The band structure shows no gap, i.e. the  $\gamma$ -phase is metallic. Also, as discussed earlier, this structure is energetically unfavourable.

## 5. Conclusions

To summarize, we have presented a first-principle study of the electronic and structural properties of the ternary compounds NaZnP, NaZnAs and NaZnSb in the Cu<sub>2</sub>Sb-type and cubic  $\alpha$ -,  $\beta$ - and  $\gamma$ -phases of the zinc-blende-type related structure. In our calculation, TB-LMTO in the LDA scheme has been used. The lattice parameters, bulk modulus and cohesive energy were calculated and are compared with the available results. From the energy–volume relations, we find that these compounds are stable in the Cu<sub>2</sub>Sb-type structure at ambient conditions and undergo a structural transition to the cubic  $\alpha$ -phase (or  $\beta$ -phase) at high pressure. Under ambient conditions in the Cu<sub>2</sub>Sb-type, NaZnP is found to be a direct-band-gap semiconductor, with the gap occurring between  $\Gamma$ -points; NaZnAs shows the band gap, but it is smaller than the semiconducting range, and NaZnSb is found to be metallic. Under ambient conditions, the  $\alpha$ - and  $\beta$ -phases of NaZnP are found to be direct band-gap semiconductors, whereas the  $\alpha$ - and  $\beta$ -phases of NaZnAs and NaZnSb are found to be semi-metallic. All three compounds are found to be metallic in  $\gamma$ -phase, which is not a favourable structure. No experimental and theoretical studies on the properties of these compounds have so far been reported. At high pressure, we observed that the band overlap metallization is found to occur for the tetragonal Cu<sub>2</sub>Sb-type and cubic ( $\alpha$ - and  $\beta$ -phase) structures of NaZnX.

## References

- [1] Wood D M, Zunger A and de Groot R 1984 *Phys. Rev. B* **31** 2570
- [2] Wei S-H and Zunger A 1986 *Phys. Rev. Lett.* **56** 528
- [3] Carlsson A E, Zunger A and Wood D M 1985 *Phys. Rev. B* **32** 1386
- [4] Bacewicz R and Ciszek T F 1988 *Appl. Phys. Lett.* **52** 1150
- [5] Madsen G K H 2006 *J. Am. Chem. Soc.* **128** 12140–6
- [6] Nowotny H and Bachmayer K 1950 *Monatsh. Chem.* **81** 488  
Nowotny H and Glatzl B 1951 *Monatsh. Chem.* **82** 720
- [7] Juza R and Hund F 1948 *Z. Anorg. Chem.* **257** 1  
Juza R, Dethlefsen W, Seidel H and Benda K 1968 *Anorg. Allg. Chem.* **356** 253
- [8] Villars P and Calverts L D *Pearson's Handbook of Crystallographic Data for Intermetallic Phases* 2nd edn, vol 1 and 4 (Materials Park, OH: ASM international, The materials international society) p 1188, 4508 & 4520
- [9] Galasso F S 1970 *Structure and Properties of Inorganic Solids* 1st edn (Oxford: Pergamon) p 95
- [10] Aramendia M A, Borau V, Jimenex C, Marinas J M and Romero F J 1995 *J. Catal.* **151** 44–49
- [11] Music A, Batista J and Levec J 1997 *Appl. Catal. A* **165** 115–31
- [12] Eisenmann B and Somer M 1985 *Z. Naturf. B* **40** 1419–23
- [13] Kabbour H, Cario L and Boucher F 2005 *J. Mater. Chem.* **15** 3525–31
- [14] Cario L, Lafond A, Morvan T, Kabbour H, Andre G and Palvadeau P 2005 *Solid State Sci.* **7** 936–44
- [15] Andersen O K and Jepsen O 1984 *Phys. Rev. Lett.* **53** 2571  
Andersen O K, Jepsen O and Sob M 1987 *Electronic Structure and its Applications* ed M Yussouff (Berlin: Springer) p 2
- [16] Skriver H L 1984 *The LMTO Method* (Heidelberg: Springer)
- [17] Hohenberg P and Kohn W 1964 *Phys. Rev. B* **136** 864



- [18] Kohn W and Sham L J 1965 *Phys. Rev.* **140** A1133
- [19] von Barth U and Hedin L 1972 *J. Phys. C: Solid State Phys.* **5** 1629
- [20] Jepsen O and Andersen O K 1971 *Solid State Commun.* **9** 1763
- [21] Birch F 1978 *J. Geophys. Res.* **83** 1257
- [22] Kalarasse F and Bennecer B 2006 *J. Phys. Chem. Solids* **67** 846–50
- [23] Kalarasse F and Bennecer B 2006 *J. Phys. Chem. Solids* **67** 1850–7
- [24] Bouhemaclou A, Khenata R and Zerarga F 2007 *Solid State Commun.* **141** 288–91